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A NOVEL ONE-POT SYNTHESIS OF 1,2-DIHYDRO-1-PHENYL-NAPHTHO [1,2-e] [1,3] OXAZIN-3-ONES

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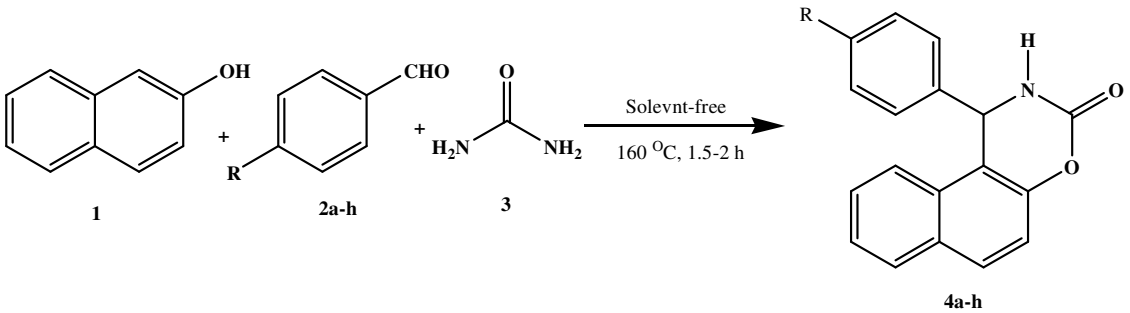
ABSTRACT
1,2-Dihydro-1-phenyl-naphtho [1,2-e] [1,3] oxazin-3-one derivatives were prepared in good yield using novel, one-pot reaction condition involving β-naphthol, urea and aromatic aldehydes under solvent-free conditions.
Keywords: 1,2-Dihydro-1-phenyl-naphtho [1,2-e] [1,3] oxazin-3-ones, aromatic aldehydes, β-naphthol, urea, solvent-free.

INTRODUCTION

With the emphasis on the search for atom-efficient transformations of easily available starting materials into complex organic molecules[1], reactions that provide maximum diversity are especially desirable. Here, expeditious domino[2] and Multicomponent[3] reactions (MCRs) have emerged as powerful strategies. Aromatic-condensed oxazinone derivatives are an important class of heterocyclic compounds, since many of these heterocyclic systems exhibit biological activities[4]. For example, naphthalene-condensed 1,3-oxazin-3-ones have been reported to act as antibacterial agents[5]. This class of compound has also been used as precursors in the preparation of phosphinic ligands for asymmetric catalysis[6].

Organic synthesis in the absence of solvent is a powerful tool for the generation of structurally diverse molecules, due to their special selectivity, the ease of set-up and work-up, arousing great interest[7]. Moreover, solvent-free reactions sometimes are faster, taking just a contact with each other. This aspect, coupled with the lower overall costs of running a reaction without solvent and no specially needed equipment, could become a decisive factor in industry.

However, in spite of their potential utility, many of these methods involve expensive reagents, strong acidic conditions, long reaction times, high temperatures, stoichiometric amount of catalysts, environmental pollution and give unsatisfactory yields. To the best of our knowledge, there have only been a few reports of the synthesis of naphthalene-condensed oxazinone derivatives in literature[8]. The condensation of 1-(α-aminobenzyl)-2-naphthol, 1-aminomethyl-2-naphthol and 2-(α-aminobenzyl)-1-naphthol as precursors with phosgene, ethyl benzimidate, 2-carboxybenzaldehyde gives naphthalene-condensed 1,3-oxazin-3-one derivatives in moderate yield[9]. In all these methods either expansive reagents or solvents are required or the reagents used are toxic and hazardous.



Scheme-1

EXPERIMENTAL

All yields refer to isolated products. Melting points were recorded on open capillaries and are uncorrected. The IR spectra were taken on Varian-640 FTIR spectrometer. The ^{1}H NMR spectra were recorded on a Varian 400 MHz spectrometer using $CDCl_3$ as solvent. The LCMS spectra were scanned on a Shimadzu LCMS-2010 EV instrument at 70 eV.

General experimental procedure for synthesis of 1,2-Dihydro-1-phenyl-naphtho [1,2-e] [1,3] oxazin-3-ones (4a-h): A mixture of β-naphthol (10 mmol), aromatic aldehydes (10 mmol), urea (15 mmol) and silica gel (60-120 mesh size, 30 % by weight) was finely mixed in round bottom flask and heated at 160 °C for appropriate time (TLC). After cooling, the reaction mixture was dissolved in ethyl acetate. The organic layer was washed with water (3 x 10 mL) and dried over sodium sulfate. The ethyl acetate was evaporated and the crude product crystallized from ethyl acetate: hexane (1:3) to afford the pure product **4a-h**.

Representative spectral data

1-(4-(Benzyloxy) phenyl)-1,2-dihydronaphtho [1,2-e] [1,3] oxazin-3-one(4e): mp: 165-168 °C; IR (ν_{max}): 3230, 3139, 1717 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-*d*6): δ = 5.01 (s, 2H, CH_2), 6.04 (d, 1 H, CH), 6.90–7.87 (m, 15H, Ar-H), LC-MS: *m*/*z* = 381 (M^+).

1-(4-(Methylsulfonyl) phenyl)-1,2-dihydronaphtho [1,2-e] [1,3] oxazin-3-one(4f): mp: 216-219 °C; IR (ν_{max}): 3230, 3139, 1717 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-*d*6): δ = 3.00(s, 3H, CH_3), 6.18 (d, 1H, CH), 7.26–7.96 (m, 10H, Ar-H), LC-MS: *m*/*z* = 354 (M^+).

1-(4-biphenyl)-1,2-dihydronaphtho [1,2-e] [1,3] oxazin-3-one(4g): mp: 230-206 °C; IR (ν_{max}): 3230, 3139, 1717 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-*d*6): δ = 6.16 (d, 1H, CH), 7.11–7.89 (m, 15H, Ar-H), LC-MS: *m*/*z* = 352 (M^+).

RESULTS AND DISCUSSION

The biological importance of these heterocycles for the development of effective, economic and sustainable synthetic methods is highly desirable. Expanding our recent efforts on developing contemporary efficient and eco-friendly synthetic methods, herein, we report a new effective, solvent-free silica catalyzed synthesis of 1,2-dihydro-1-phenyl-naphtho [1,2-e] [1,3] oxazin-3-ones in short reaction of time (1-2 h).

The reaction of β-naphthol (10 mmol), benzaldehyde (10 mmol) and urea (15 mmol) was heated to stirred at 160 °C up to 12 h, but there was no formation of desired product (reaction was monitored by thin layer chromatography) (Scheme 1), when we added silica-gel (60-120 mesh) (30 % by wt.), the reaction was completed in 1.5 h without any added solvent. It clearly indicates that acidity of silica gel and temperature increases the rate of reaction and deliver desired compound in quantitative yield.

Also we tried same reaction with silica gel at different temperature and we found that 160 °C was optimum temperature to gave the desired compound in quantitative in short reaction time (Table 1). After the optimizing reaction temperature and catalyst loading, we synthesized different heterocycles by using 4-substituted benzaldehydes (Table 2). Present protocol tolerates both electron donating group as well as electron withdrawing groups on benzaldehyde.

CONCLUSION

In conclusion, we have developed an efficient method for the synthesis of 1,2-dihydro-1-phenyl-naphtho [1,2-e] [1,3] oxazin-3-ones from β-naphthol, urea and aromatic aldehydes under solvent-free conditions. This method represents a simple procedure involving mild reaction conditions, and has general applicability. It avoids hazardous organic solvents and toxic catalysts and typically provides nearly quantitative yields of products.

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Table-1: Effect of temperature for synthesis of 4a:

Entry	Temp. (°C)	Reaction Time (h)	Yield (%)
1.	30	24	00
2.	60	24	05
3.	100	24	60
4.	130	12	80
5.	160	1.5	80

Table-2: Synthesis of 1, 2-Dihydro-phenyl-naphtho [1, 2-e] 1, 3] oxazin-3-ones (4a-h):

Entry	R	Time (h)	Yield (%)	Mp °C
4a	H	1.5	80	217-218 (218-220)[10]
4b	4-Br	1.8	78	222 (220-223) [10]
4c	4-OMe	1.5	71	185 (185-188)[10]
4d	4-F	1.5	73	201-203 (202-204)[10]
4e	4-$PhCH_2O$	2.0	70	165-168
4f	4-$MeSO_2$	1.8	75	216-219
4g	4-Phenyl	1.5	72	203-206
4h	4-OH	1.5	70	182 (180)[10]

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